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DIELECTRIC ANALYSIS OF THE CURE OF THERMOSETTING
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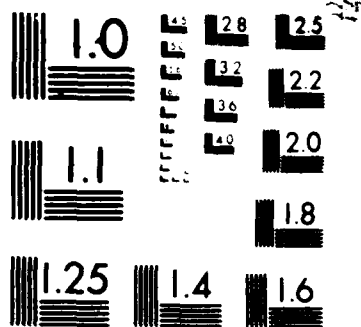
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**DIELECTRIC ANALYSIS OF THE CURE OF
THERMOSETTING EPOXY/AMINE SYSTEMS**

by

**Sue Ann Bidstrup, Norman F. Sheppard, Jr.,
and Stephen D. Senturia**

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Electrical Engineering and Computer Science
Microsystems Technology Laboratories
Cambridge, MA 02139

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A low molecular weight epoxy resin was cured isothermally with an aromatic amine hardener, and the ionic conductivity was measured as a function of frequency, reaction time and cure temperature. At specific stages in the cure small samples from the reacting mixture were quenched, and then analyzed for the glass transition temperature and epoxy group conversion by differential scanning calorimetry. In this manner changes in ionic conductivity could be directly correlated with the build-up of network structure during polymerization. The conductivity was modeled as a function of the cure temperature and the		

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Co-172 ABSTRACT

cure-dependent glass transition temperature using a Williams-Landel-Ferry (WLF) relation. The behavior of the conductivity for an isothermal curing system was found to be consistent with the WLF behavior of a set of neat epoxy resins of various T_g , but with changing temperature. An empirical DiBenedetto relation was used to correlate changes in epoxy conversion with the glass transition temperature. Combining the DiBenedetto model with the WLF relation for conductivity, the ionic conductivity can be predicted as a function of the epoxy group conversion. (keywords)

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INTRODUCTION

Monitoring the structural build-up of a thermosetting polymer during cure is difficult. During polymerization, thermosets undergo large changes in rheological properties. Few techniques are available which can characterize the polymer in both the liquid and rubbery regions. As a result, the measurement of dielectric properties has been widely used to study the cure of thermosets [1] since it is one of the few methods that can follow the complete transformation from liquid resin to glassy solid. However, the relationship between the dielectric properties and structural changes has not been fully established. A better understanding of this relationship would be of considerable value in the application of dielectric measurements to thermoset process monitoring and control.

Ionic conductivity can be particularly useful as a monitor of thermoset cure. Not only does it become increasingly sensitive to changes in the glass transition temperature as the end of cure is reached but it can almost always be measured, even in the presence of dipole effects, by decreasing the measurement frequency [1]. In addition, a Williams-Landel-Ferry (WLF) relationship [2] between the ionic conductivity and the cure temperature and the glass transition temperature has been established [3,4]:

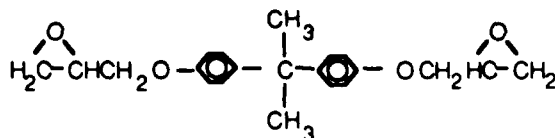
$$\log a_T = \log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (1)$$

where the shift factor a_T is defined as the ratio of conductivity at temperature T to the conductivity measured at the glass transition temperature T_g . C_1 and C_2 are constants, originally thought to have universal values, but it is now accepted that these constants are material dependent. Sheppard and Senturia [3,4] have found that the temperature dependent conductivities of a homologous series of DGEBA epoxy resins (without hardener) of varying molecular weights obey WLF relations. Analysis of this neat resin data revealed that while the WLF constant C_1 is relatively independent of the molecular weight of the resin, the C_2 constant and the reference conductivity, $\log \sigma(T_g)$, can be represented by a simple linear dependence on the T_g of the material. A similar behavior of C_2 and $\sigma(T_g)$ was used to model ionic conductivity changes during the cure of a DGEBA resin with a tetrafunctional amine [5]. The results showed that the behavior of σ with a changing T_g during isothermal cure is consistent with the WLF behavior of a set of neat epoxies of fixed T_g but with changing temperature. However, additional work was required before specific values could be obtained for the WLF constants.

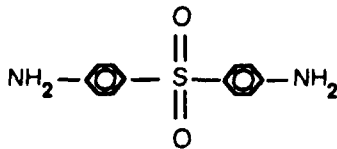
In this study, the relation between ionic conductivity, cure temperature and the glass transition temperature for a low molecular weight epoxy cured with an aromatic amine hardener is explored further. The conductivity was measured as a function of reaction time and cure temperature. At specific stages in the cure, small samples from the reacting mixture were quenched and then analyzed for T_g and the degree of epoxy conversion by differential scanning calorimetry (DSC). In this manner, the change in dielectric properties could be directly correlated with the build-up of network structure during polymerization. The ionic conductivity was modeled as a function of the cure temperature and T_g using a WLF relation. The behavior of σ with changes in the degree of conversion was also explored.

EXPERIMENTAL

The system used for this study consists of diglycidyl ether of bisphenol A (DGEBA) cured with 4,4' diaminodiphenyl sulfone (DDS):



Diglycidyl Ether of Bisphenol A
(DGEBA)



Diamino-Diphenyl Sulfone
(DDS)

Commercial grade DGEBA was obtained under the trade name DER 332 (Dow) and was purified by recrystallization. The curing agent DDS was used as received (~99% purity) from the Aldrich Chemical Company. Samples were prepared by mixing purified DGEBA crystals with a stoichiometric amount of DDS. The mixture was then heated in a 120°C oil bath and stirred rapidly for approximately one minute until both components were dissolved. Then the sample was quickly removed from the oil bath and quenched in ice. Samples were used immediately after preparation.

The dielectric measurements were performed using a Micromet Instruments Eumetric System II Microdielectrometer, which utilizes a silicon integrated circuit sensor having a comb electrode pattern, amplifying circuitry and a semiconductor diode for temperature measurement. The electrode area of the microdielectrometry sensor is 2 x 3.5 mm. A single drop of the epoxy-amine material was placed on the dielectric sensor surface. In addition, small amounts (10-20 mg) of epoxy-amine sample were loaded into hermetically sealed aluminum DSC pans. The sensor and DSC pans were placed into a tray and then inserted in a Carver Model 2518 hydraulic lab press preheated to the cure temperature. This press was used only to provide a conveniently shaped and accessible isothermal environment. The cure was performed under a blanket of nitrogen. The permittivity ϵ' and the dielectric loss factor ϵ'' were measured at even decades of frequency over a range of 1 - 10,000 Hz throughout the cure. The conductivity σ was determined from the loss factor, at frequencies where a log-log plot of the loss factor versus frequency has a slope of -1, using the relation

$$\epsilon'' = \sigma / \omega \epsilon_0 \quad (2)$$

where ω is the angular frequency and ϵ_0 is the permittivity of free space (8.85×10^{-14} Farads/cm). At particular stages during the cure, some of the DSC pans were removed from the press and quenched by placement in a -20°C freezer.

The glass transition temperature and epoxy group conversion for these quenched samples were measured using a Perkin-Elmer DSC 4. The glass transition temperature was determined by a temperature scan of the sample at a rate of 10°C/min. T_g was defined as the midpoint in the transition curve. For conversion analysis, the DSC pans were scanned at 5°C/min from 100°C to 320°C, and the residual heat of reaction ΔH_r (i.e. the heat evolved during completion of crosslinking) was measured. The total heat of reaction ΔH_t for the epoxy-amine cure was determined by placing an unreacted sample in the DSC pan and measuring the heat evolved during a temperature scan. Assuming the only reaction occurring during the cure is between the epoxy group and an amino-hydrogen, the degree of conversion α was calculated from [6]:

$$\alpha = \frac{\Delta H_t - \Delta H_r}{\Delta H_t} \quad (3)$$

The precision of the determination of α was limited by baseline subtraction errors, and thus the data for α must be considered preliminary. However, the data can be used to examine approximately how σ and α are related.

RESULTS AND ANALYSIS

Figure 1 presents the ionic conductivity changes during the cure of DGEBA with DDS at isothermal cure temperatures ranging from 135°C to 188°C. This behavior is similar to that reported previously [1, 3-5]. During cure, σ decreases slowly at first, then more rapidly. As the cure proceeds, an inflection point is observed, which marks the slowing of the cure reaction. The shapes of the curves at different cure temperatures are similar, but accelerated in time at higher cure temperatures. The T_g data from the DSC analysis at particular stages in the polymerization are shown in Figure 2 as a function of cure time and temperature. The correlation between the measured values of σ and T_g is shown in Figure 3. The solid lines represent the best fit of the WLF model as described below.

For a series of neat epoxy resins with varying molecular weight, Sheppard [3,4] has found the the ionic conductivity can be modeled with a pseudo-WLF equation assuming a linear dependency of C_2 and $\log \sigma(T_g)$ with T_g . Therefore the WLF relation (Equation 1) can be rewritten:

$$\log a_T = \log \sigma(T) - [C_5 + C_6 T_g] = \frac{C_1 (T - T_g)}{C_3 + C_4 T_g + (T - T_g)} \quad (4)$$

where $C_5 + C_6 T_g$ replaces $\log \sigma(T_g)$ and $C_3 + C_4 T_g$ replaces C_2 . The data of Figure 3 were fit to Equation 4 by a nonlinear least-squares method. The resulting WLF constants are shown in the right hand column in Table 1.

TABLE 1
WLF CONSTANTS

	PURE DGEBA RESINS [4]	DGEBA-DDS CURE
C ₁	10.5	9.0
C ₃	-109	-194
C ₄	.58	.73
C ₅	-19	-18
C ₆	.013	.013

The corresponding constants obtained from Sheppard's neat-epoxy data are shown in the left hand column. The agreement between the WLF constants is very good, especially considering the large number of constants and the form of the WLF equation. Figures 3 and 4 illustrate the least-square fit of WLF model to the ionic conductivity data at isothermal cure temperatures ranging from 135°C to 188°C. These results support the idea [5] that behavior of σ for isothermally curing systems with changing T_g is consistent with the WLF behavior of a set of neat epoxy resins of various T_g but with changing temperature. Work is now in progress to reduce the number of fitted WLF constants by measuring $\sigma(T_g)$ directly.

The establishment of the relation between ionic conductivity and the conversion of epoxy groups would be extremely valuable for the application of microdielectrometry as a cure monitor. Towards the end of the cure reaction, the degree of conversion (α) is very insensitive to cure time, and is difficult to measure accurately. However, small changes in the conversion can result in large changes in mechanical properties of the polymer. Ionic conductivity changes remain sensitive to structural changes, even at the end of cure, and hence, offer the promise of being sensitive to small changes in α late in the cure.

To correlate ionic conductivity with conversion, an expression is needed for the relationship between T_g and α . Adabbo [7] and Enns [8] have used a DiBenedetto equation [9] to relate T_g of epoxy cure systems to α . This model takes the form

$$\frac{T_g - T_{g,0}}{T_{g,0}} = \frac{(E_x/E_m - F_x/F_m)\alpha}{1 - (1 - F_x/F_m)\alpha} \quad (5)$$

where E_x/E_m is the ratio of lattice energies for crosslinked and uncrosslinked polymer, F_x/F_m is the corresponding ratio of segmented mobilities and $T_{g,0}$ is the glass transition temperature of the unreacted material. The values of E_x/E_m and F_x/F_m have been estimated for this resin system [3,4] to be 0.3 and 0.18, respectively. The relation between α and T_g assuming these constants is plotted in Figure 5, along with the DSC data obtained on the quenched samples. Although there is considerable scatter in the conversion data, there is general agreement with the

DiBenedetto model. Combining this model with the WLF relation for conductivity (Equation 3), the ionic conductivity can be predicted as a function of the epoxy group conversion. The results are shown in Figure 6. Work is in progress to test this relation by simultaneously measuring ionic conductivity and epoxy group conversion during an isothermal cure.

ACKNOWLEDGEMENT

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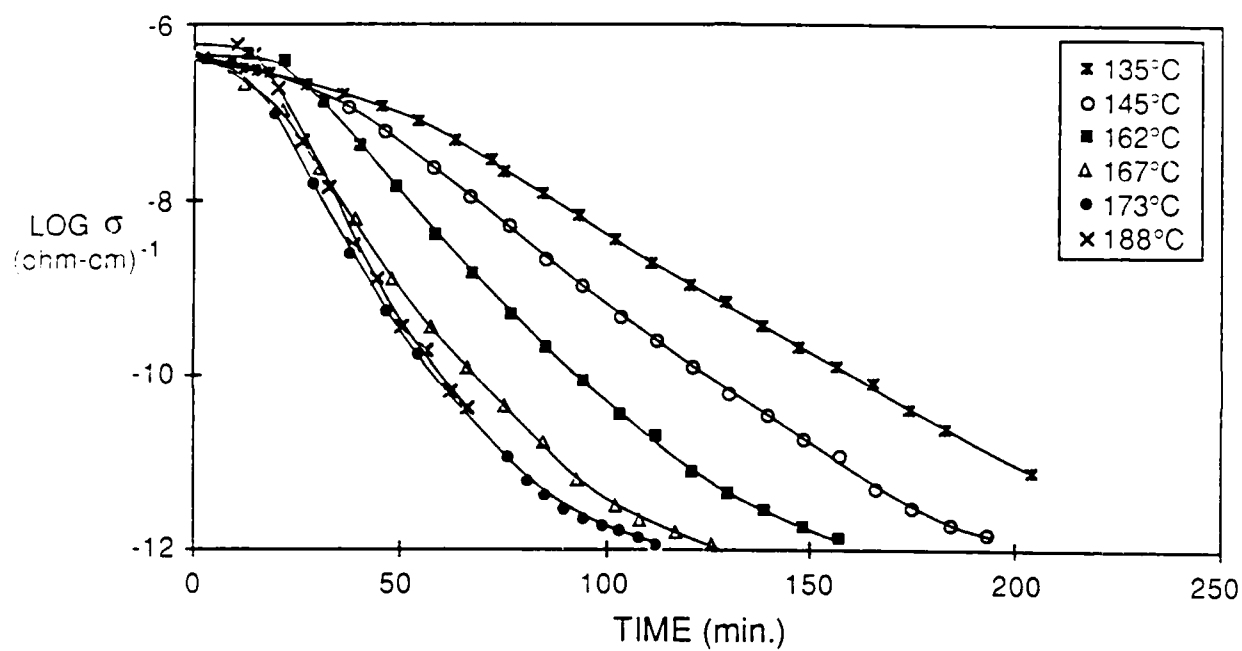


Figure 1. Experimentally measured conductivity versus cure time for DGEBA resin cured isothermally with DDS.

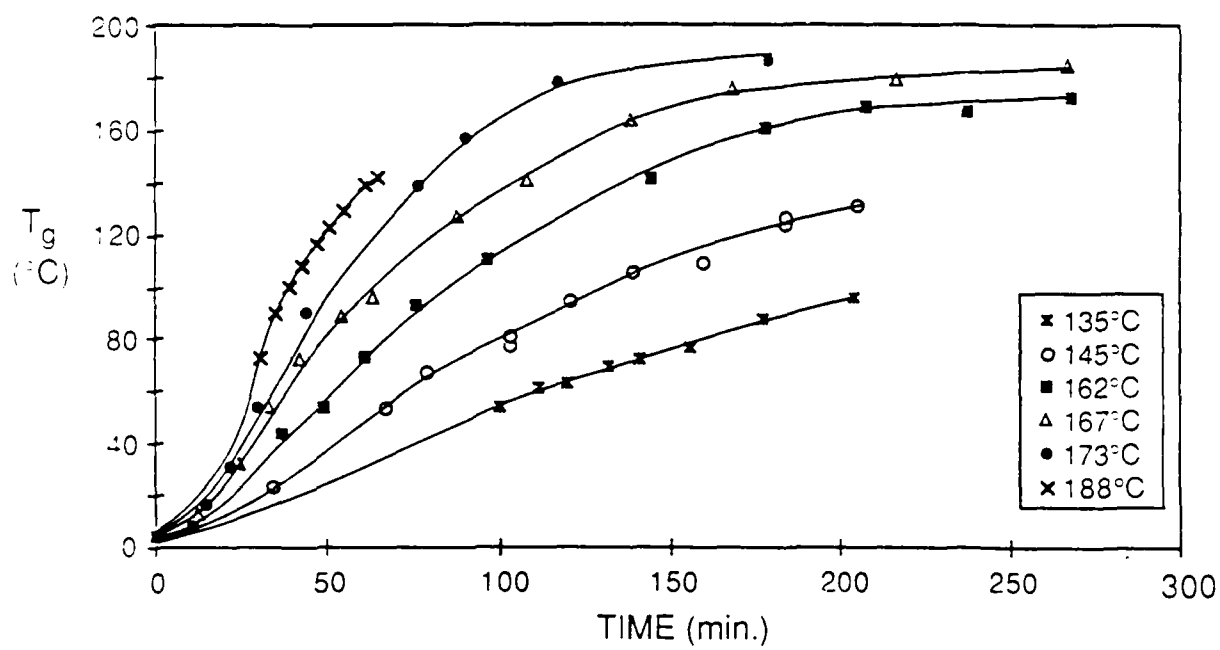


Figure 2. Measured glass transition temperature versus cure time for DGEBA resin cured isothermally with DDS.

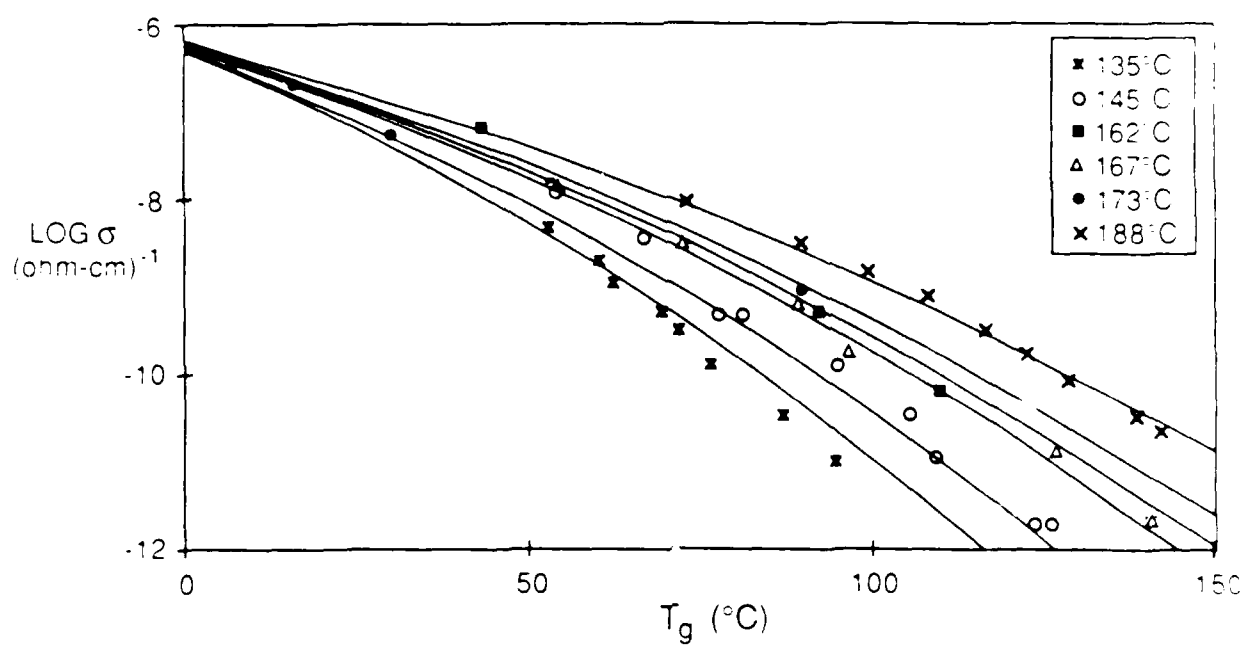


Figure 3. Conductivity versus the glass transition temperature for the DGEBA resin cured isothermally with DDS. The solid curves represent the best fit of the WLF mode

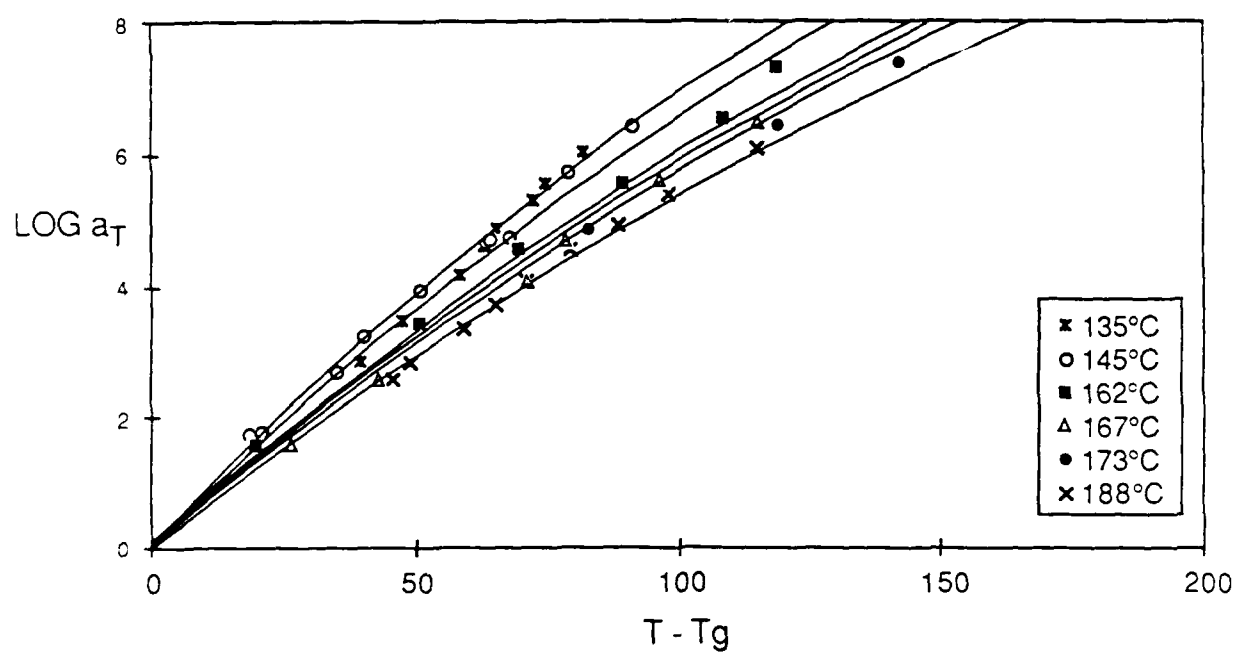


Figure 4. The shift factor versus the difference between the cure and the glass transition temperatures for the DGEBA resin with DDS. The solid curves represent the best fit of the WLF model.

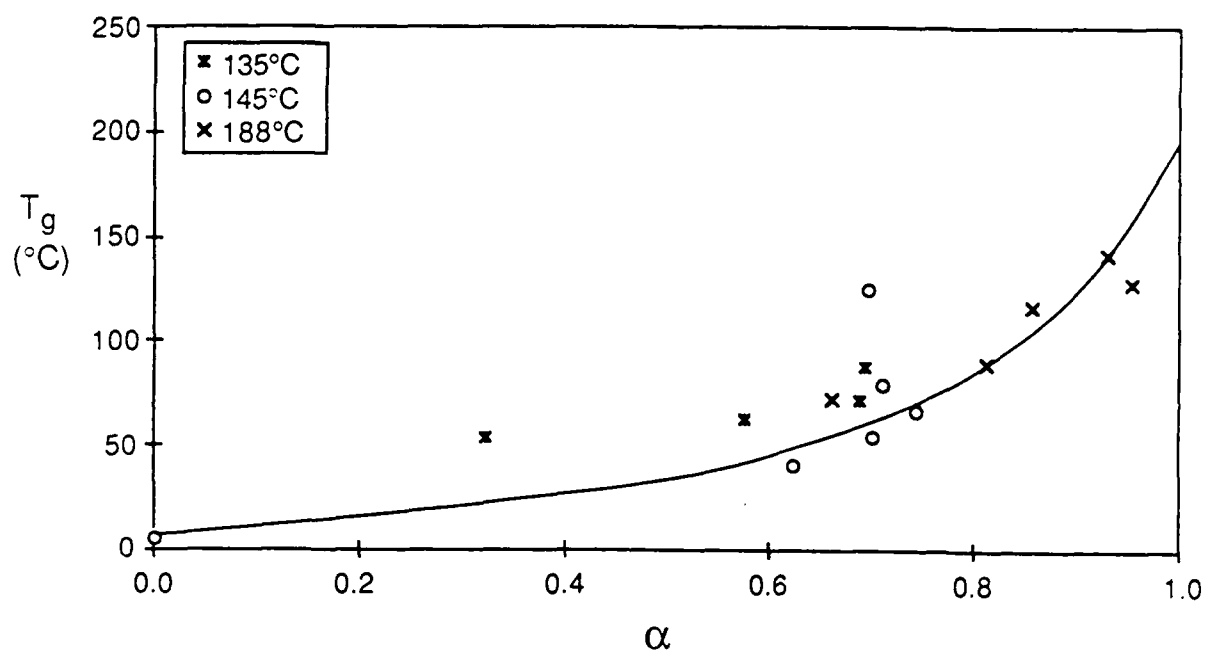


Figure 5. The glass transition temperature versus the degree of conversion for the isothermal cure of DGEBA with DDS. The solid curve represents the DiBenedetto equation (Equation #5) assuming $E_x/E_m = .3$ and $F_x/F_m = .18$.

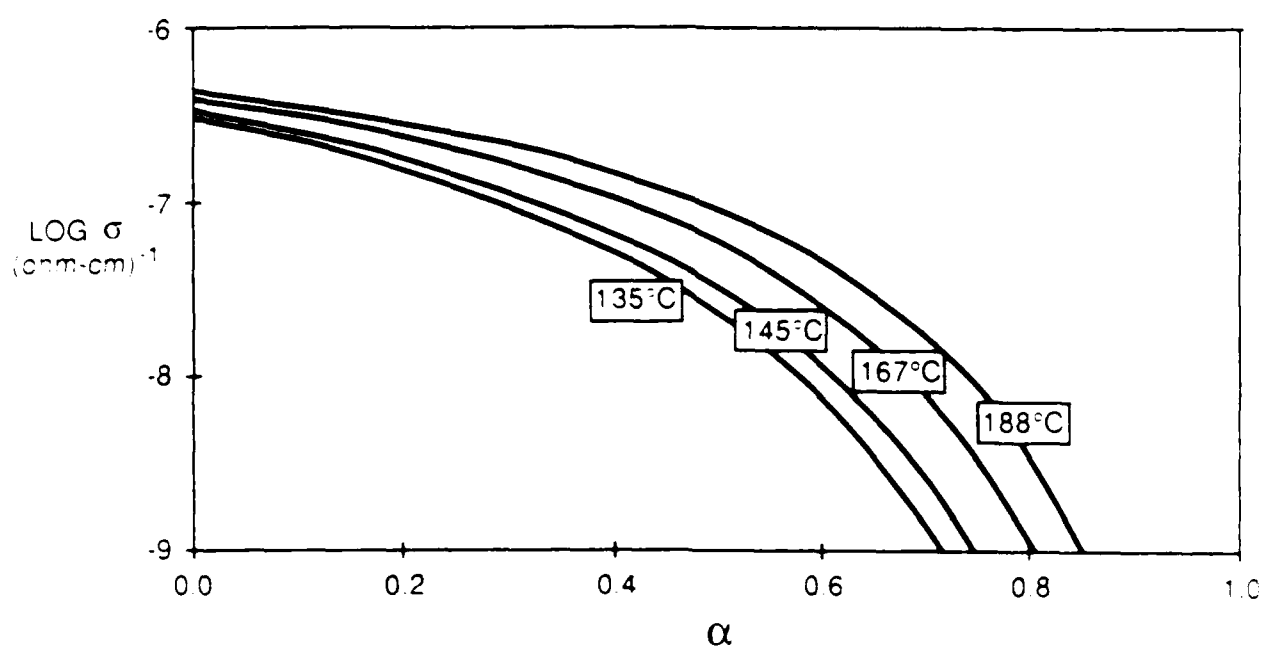


Figure 6. Combined WLF-DiBenedetto model to predict the relationship between ionic conductivity and the degree of conversion.

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